

PATENT SPECIFICATION

Inventor: CONRAD SCHOELLER

811.135



Date of Application and filing Complete Specification Oct. 31, 1956

No. 33201/56.

Complete Specification Published April 2, 1959.

Index at acceptance: —Classes 2(5), R27K1B, R27K1C(7:8:12:16); 2(6), P4A, P4C(5:13A:14A:14B:15:20B), P4D3B(1:3), P4(K11:S2), P6A, P6C(5:13A:14A:14B:15:20B), P6(D1:K11:S2), P7A, P7C(5:13A:14A:14B:15:20B), P7(D2A1:K11:S2), P8A, P8C(5:13A:14A:14B:15:20B), P8D(1A:1B:2A:2B2:3A:4), P8(K11:S2), P10A, P10C(5:13A:14A:14B:15:20B), P10(D1A:K11:S2), P11A, P11C(5:13A:14A:14B:15:20B), P11D2A, P11K(6:7:8:10), P11S2; and 81(1), L4.

International Classification: —A61k. C08f, g.

COMPLETE SPECIFICATION

Products Containing Polymerised N-Vinyl Lactams and Polyalkylene Imines

5 We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESSELLSCHAFT, a Joint Stock Company organised under German Law, of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to products containing polymerised N-vinyl lactams and polyalkylene imines.

15 One object of the invention is the production of products for the cosmetic and pharmaceutical industries.

Another object of the invention is the production of adhesives, binding agents and impregnating agents for fibrous materials of all kinds.

20 Yet another object of the invention is the production of varnish-like coating agents.

A further object of the invention is the production of textile assistants.

25 A further object is the production of films or coatings on supports by the application thereto by dipping, brushing or spraying of solutions of the two components.

30 These and other objects have been achieved by allowing a mixture of a polymer which has been prepared from at least one N-vinyl lactam, if desired together with another polymerisable compound, and a polyalkylene imine or a polyalkylene imine derivative to stand in the presence of water or an organic solvent, preferably miscible with water, for some time at room temperature, or by heating said mixture in the presence of water or an organic solvent or by eliminating the solvent by evaporation or *in vacuo*. By these steps there

are obtained products the properties of which differ from those of each of the single components. However, the mechanism of this phenomenon has not so far been elucidated.

40 The term polymerised N-vinyl lactams is intended to include polymers and copolymers of, for example, N-vinyl-pyrrolidone, N-vinyl caprolactam or N-vinyl caprylic lactam. The vinyl lactams may also bear substituents on the carbon atoms of the lactam ring. Such vinyl lactams are the alkyl derivatives, for example N-vinyl lactams substituted by methyl or ethyl groups. The copolymers may be prepared from N-vinyl lactams with one another or from one or more of the N-vinyl lactams with other polymerisable compounds. The 45 proportion of N-vinyl lactam in the copolymers may amount to down to 10% by weight or less with reference to the total mixture. Among polymerisable compounds which can be polymerised together with the vinyl lactams there may be mentioned for example the vinyl halides, such as vinyl chloride and vinylidene chloride, the vinyl esters, such as vinyl formate, acetate, propionate, isopropionate and vinyl esters of higher carboxylic acids, for example of fatty acids. Other suitable vinyl 50 derivatives for the copolymers are the vinyl ethers, such as vinyl methyl, ethyl, propyl or isopropyl ethers and also the vinyl ethers of higher alcohols, for example of fatty alcohols. Styrene and substituted styrenes can also be used for the production of the copolymers with vinyl lactams.

55 Instead of these vinyl derivatives, or additionally to these vinyl derivatives, there may also be used in the copolymers with N-vinyl lactams, other polymerisable compounds, as for example acrylic acid and its derivatives. 60 65 70 75

Examples of these are methacrylic acid, acrylic acid ethers, methacrylic acid esters, acrylonitrile, acrylamide and methacrylamide.

The molecular weight of the polymerised vinyl lactams capable of being used according to this invention can be as high as desired. For example poly-N-vinyl-pyrrolidones may be used having the molecular weights 16,000, 30,000, 220,000, or 750,000, or poly-N-vinyl caprolactams of the molecular weight 150,000. Polymers with a molecular weight of 100,000 to 200,000 are preferred. In the case of the copolymers it is important that they should be soluble in water or in organic solvents which are miscible with water. If copolymers are produced from N-vinyl-pyrrolidone or N-vinyl caprolactam and such substances as do not by themselves yield water-soluble polymers, it will in general be sufficient for obtaining a water-soluble copolymer if at least 40% of either N-vinyl-pyrrolidone or N-vinyl caprolactam are polymerised in.

Polyalkylencimines for use according to the invention can be prepared from ethylene imine according to known methods.

The molecular weight of the polyalkylene imines may amount to 2000 to 100,000, more preferably about 10,000 to 30,000.

The polyalkylene imines also may contain in the molecule high molecular weight amines, as for example stearylamine or 2'.4'-diaminoazobenzene-sulphonamide-(4) obtainable by reacting ethylene imine with said amines. Salts of the polyalkylene imines can also be used for the purposes of the invention.

The relative proportions in the products containing polymerised vinyl lactams and polyalkylene imines according to this invention may amount to 100:0.5 to 100:10 parts by weight. Relative proportions of 100:3 to 100:6 parts by weight are preferred. Depending on the chemical and physical properties of the components, namely of the polymerised vinyl lactams and the polyalkylene imines, products may be prepared according to this invention for which there are a great variety of possibilities of use.

Some of the possible methods of procedure for the productions of the products according to this invention are given in the following description. It is emphasised, however, that the present invention is not limited to these specific methods of procedure.

Water-soluble polymerised N-vinyl lactams, for example those which contain at least 40% of N-vinyl-pyrrolidone, are converted into an about 3 to 50% aqueous solution. To this solution there is then added the necessary amount of polyalkylene imine as an about 10 to 50% aqueous solution. It is heated for some minutes, for example 1 to 20 minutes, at 30° to 60° C. or allowed to stand at room temperature for a longer period, for example 1 to 3 hours. The products according to this invention can also be obtained by allowing the

solvent to evaporate. In this case the end product is obtained as a pulverisable mass.

In the case of N-vinyl lactams which are not soluble in water, organic solvents are used, preferably those which are miscible with water. For this purpose there come into question alcohols, such as methyl, ethyl, propyl or isopropyl alcohol or polyglycol ethers. The water-soluble polymerised N-vinyl lactams may also be reacted in the organic solvents. Solutions of polymerised N-vinyl lactams with a concentration higher than 50% by weight are too difficult to handle for combination with the polyalkylene imines.

Another possibility for the reaction consists in adding the finely divided or pulverised polymerised N-vinyl lactam to an aqueous or, for example, aqueous-alcoholic or alcoholic solution of the polyalkylene imine, and then following the above procedure, i.e. heating it or allowing it to stand for a longer time at room temperature, preferably while stirring.

An indication that the end products have been obtained is given when the solution of the initial components becomes viscous or gelatinous. The end products dry to films which, as compared with the polymerised N-vinyl lactams used as initial materials, have a higher waterproofness, smaller swelling power and greater hardness, and are moreover less sticky.

Yet another possibility for obtaining the products according to this invention consists in drying the solution of the polymerised N-vinyl lactams and the polyalkylene imines.

In the ways described, depending on the nature of the components, there are obtained water-soluble, water-swellaable or water-insoluble products. The products can be converted into high molecular solutions. Naturally carboxyl groups which are contained in the macromolecules of the polyvinyl lactams increase the tendency of the products to be soluble in water. The carboxyl groups can be introduced into the molecule by copolymerisation of the vinyl lactams for example with acrylic acid, by hydrolysis or by oxidation of the polyvinyl lactams.

In preparing the products according to this invention mixtures of polymerised lactams and mixtures of polyalkylene imines can also be used.

The products obtainable according to the process of this invention, whether it be with or without additional substances, have good stability in storage and are durable. The products are extensively resistant to the influence of micro-organisms. In contrast to natural products, their composition is accurately reproducible. The solutions of the products are substantially compatible with acids and alkalis. They are substantially insensitive to reducing or oxidising additions. Films produced with these products, for example on the human hair, adhere very firmly although they

are not hard. The products are therefore eminently suitable as fixing agents in cosmetics and in hair treatment, and also as adhesives or depot agents in medicine.

The products according to this invention may also be used, *inter alia*, for the following purposes: For improving the fixation of agents for combatting pests, for the production of films or coating for the purposes of the photo-chemical industry, as preparation agents and sizing agents in the manufacture of synthetic fibres, fabrics, knitted goods, for the improvement of the properties of textiles, leather, paper, as assistants in dyeing and printing works or as binding agents or film-forming agents for water-soluble or water-insoluble dyestuffs in the dyeing of natural or synthetic materials or their intermediates, as binding agents or adhesives, for example for paper, textiles, medical plaster, surgical dressings, leather, artificial leather, linoleum, wood, glass, metal, as thickening agents and protective colloids.

In the production of solutions and films there may also be co-employed for example softening agents, organic solvents, uncoloured or coloured organic or inorganic pigments, metal salts, dyestuffs, disinfectants, pharmaceutical substances, contact insecticides, perfumes, hydrophobing agents, adhesives, plastics, resins and their initial materials, and also additional reaction partners for the polymeric alkylene imines.

The following examples will further illustrate this invention but the invention is not restricted to these examples. The parts specified in the examples are parts by weight.

EXAMPLE 1.

5 parts of a 20% aqueous solution of a polyvinyl pyrrolidone of molecular weight about 30,000 are mixed with 10 parts of a 10% aqueous solution of a polyethylene imine of about molecular weight 20,000 and the mixture heated at 40° to 50° C. for 15 minutes. A jelly which is difficultly soluble in water is obtained.

EXAMPLE 2.

10 parts of polyvinyl pyrrolidone of molecular weight 300,000 or 700,000, 0.5 part of polyethylene imine of about molecular weight 20,000 and 0.5 part of glycerine are dissolved in 89 parts of water and the solution heated until the water has evaporated. The reaction product obtained yields a film which is not dissolved in water until after action for 5 hours. On the contrary a film prepared without the use of polyethylene imine is dissolved in water even after 15 to 20 minutes. A film prepared according to this example is also surprisingly stable to hot water and to soda solution.

EXAMPLE 3.

About 2 to 5% of polyethylene imine of the approximate molecular weight 20000 are

added to a 10% aqueous solution of polyvinyl pyrrolidone of the molecular weight about 700,000. A highly viscous solution forms with which wood surfaces can be stuck together much more firmly in a manner much more resistant to water than with polyvinyl pyrrolidone alone. It is preferable to press together for some hours at room temperature the wood surfaces which have been brushed with the solution. Paper foils may also be glued well by brushing them with the solution of the said product, pressing them together and drying for about 30 minutes at 90° C. Organic solvents, for example isopropyl alcohol, may also be used instead of water.

An adhesive which is also waterproof is obtained from a copolymer of 60 parts of vinyl pyrrolidone and 40 parts of acrylic acid which has been neutralised with caustic soda solution and reacted with about 5% of polyethylene imine and 5% of the reaction product of about 60 mols of ethylene imine and 1 mol of stearylamine hydrochloride.

EXAMPLE 4

To a 10% alcoholic solution of polyvinyl caprolactam there are added 5% of polyethylene imine (with reference to the polyvinyl caprolactam). After evaporating the alcohol, a colourless transparent film is obtained which is stable in a 3% aqueous soda solution and does not swell. On the contrary a film prepared without the use of polyethylene imine has swollen even after 30 minutes.

The product from the two components need not be prepared in a reaction vessel, but can also be prepared on a substrate, for example of wood or textile material, which is to be treated for the said purposes of use. For example the two components may be applied separately by brushing or dipping in substance or in solution and the substrate thus prepared subjected for example to calendering, steaming or infra-red irradiation.

EXAMPLE 5

An aqueous solution of 5% of polyvinyl pyrrolidone of approximate molecular weight 28000 and 0.3 to 0.5% of polymeric ethylene imine is prepared. Hair brushed with this solution is rendered extremely stiff after drying. If the treated hair is then laid in water for one minute and dried, the stiffening effect is completely retained. If the experiment is carried out with the same amount of polyvinyl pyrrolidone, but without the addition of the polymeric ethylene imine, a similar stiffening effect is achieved but it is completely removed by the said water test, i.e., the effect is not stable to moisture or rain.

The water-stable stiffening may when necessary be removed from the hair by a soap treatment; on the contrary this is not possible with hair which has been given a water-stable stiffening with resins.

- 5 If the hair is treated or sprayed with a 90% alcoholic solution which contains 5% of polyvinyl pyrrolidone of about molecular weight 700,000 and 0.3 to 0.5% of polymeric ethylene imine, it exhibits similarly after drying a waterproof stiffening effect and also an improvement in lustre.

EXAMPLE 6

- 10 If 5% of a copolymer of equal parts of vinyl pyrrolidone and vinyl propionate of molecular weight about 150,000 are dissolved in pure ethyl alcohol and 0.2% of polymeric ethylene imine is added, a film of very good waterproofness is obtained. A preparation consisting of
15 17.5 parts of absolute alcohol, 2 parts of the said copolymer, 0.1 part of polymeric ethylene imine, 0.2 part of shellac or a resin prepared from colophony by reaction with an unsaturated carboxylic acid, 0.2 part of a perfume composition and 80 parts of a propellant gas, is
20 especially suitable as a stiffening and fixing agent when sprayed on human hair.

WHAT WE CLAIM IS:—

1. Products containing polymerised N-vinyl lactams and polyalkylene imines which products are obtained by allowing a mixture of a polymer which has been prepared from at least one N-vinyl lactam, if desired together with another polymerisable compound, and a polyalkylene imine or a polyalkylene imine derivative to stand in the presence of water or an organic solvent, preferably miscible with water, for some time at room temperature, or by heating said mixture in the presence of water or an organic solvent or by eliminating the solvent by evaporation or *in vacuo*. 25
2. Products containing polymerised N-vinyl lactams and polyalkylene imines when obtained according to any of the foregoing examples. 30
3. The process for preparing the products substantially as described in any of the foregoing examples. 35 40

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1959.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.